

Quantification of Rock Porosity Changes before and after Freezing

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Abstract

Petroleum exploration and production from shale formations have gained great momentum throughout the world in the last decade. Producing hydrocarbons from shale is challenging because of the low porosity and permeability thus requiring fracturing completion, whose successes rely on the knowledge of rock properties and in-situ stress. It is imperative to investigate and understand the rock geomechanics in the shale formations. To the best of our knowledge, the freezing method is the most successful approach to prepare the shale core sample for lab test. Unfortunately, the preparation of shale core plugs includes the procedure of freezing that alters the rock properties. This paper quantifies the difference in rock porosity before and after the freezing based on data from numerous rock experiments. Porosities of different rocks had been measured before the rock samples were put into the freezer for freezing. After the rock porosities have been measured, the core samples were stored in the freezer. Then the porosities of core samples after freezing were measured. With above experiments, a porosity database was built and a non-linear regression method was used to derive correlations to quantify the changes in the porosity due to freezing. Our correlations is applicable for geoscientists and engineers to adjust the shale property to the values before freezing. With the correct porosity, more accurate original oil in place can be estimated and more reliable permeability from porosity-permeability correlation can be calculated. Eventually, the estimated ultimate recovery can be evaluated confidently. Results of this study can also be applied to other areas such as underground storage of liquid natural gas (LNG), underground energy storages, etc.

Keywords

Rock Porosity; Freezing of Rock; Rock Porosity Change

Introduction

After more than one hundred years of development and production, conventional oil and gas reserves are

depleting significantly on a worldwide basis. In order to meet the increasing demand of hydrocarbon energy, it is essential to develop unconventional resources. Shale oil and gas becomes crucial supplements to the conventional hydrocarbon reservoirs. Petroleum exploration and production from shale formations have gained great momentum throughout the world in the last decade. Producing hydrocarbons from shale is challenging because of the low porosity and permeability thus requiring fracturing completion, whose successes rely on the knowledge of rock properties and in-situ stress. It is imperative to investigate and understand the rock geomechanics in the shale formations. Although numerous investigations have been conducted to better understand rock properties of shale and the fluids properties and flow behavior in shale under reservoir condition, the progresses in rock and fluid characterizations and fluid-rock interaction description are impeded by the availability of experimental data on shale sample. Our literature review indicates that numbers of core analysis on shale are limited due to the difficulty in preparing shale plug from drilling cores. The brittle nature of shale makes the successful rate of preparing plug from drilling core lower. Usually, the successful rate ranges from 0 to 10%. Another element that contributes to the rare experimental data of shale is the low porosity and extremely low permeability feature of shale. Conventional methods to analyze core porosity and permeability do not work or cannot be afforded due to expensive cost and time consuming when they are applied to analyze shale. To overcome the sampling difficulty, the freezing sample method is used in preparing the plug for core analysis. It is undoubted that the freezing will alter the rock texture and

structure thus the rock properties such as porosity and permeability, but to the best of our knowledge, it is the most successful approach to prepare the shale core sample for lab tests. Therefore, to obtain original rock properties, it is imperative to quantify the difference before and after the freezing. In this study, the way the porosity changes during freezing process has been investigated.

The effect of temperature on elastic properties of porous materials has been investigated by researchers of different fields, including petroleum engineering, civil engineering, and chemical engineering. For the purposes of this study, we reviewed the studies that focused on the porosity change as a function of temperature. These researches can be classified into two main categories according to temperature below and above ice melting point (or water freezing point). The first category targeted temperature higher than ice melting point (or water freezing point); while the other investigated temperature is lower than ice melting point under which the expansion of ice becomes the main cause that alters the rock properties. Followings list some important researches identified as milestones that advance the understanding of effect of temperature on rock properties.

First Category: Temperature Higher than Ice Melting Point

Somerton et al. (1965) studied the thermal effect on sandstone in the range of 400 to 800°C, whose works showed that large changes in physical properties occur as a result of heating and subsequent cooling to room temperature. They believed that the alteration of rock properties is caused by a number of reactions occurring during heating, which include the differential thermal expansion of the quartz grains, the dissociation of dolomite at higher temperatures, and the “firing” of clays at lower temperatures. Sanyal et al. (1974) investigated the effect of temperature on petrophysical properties of reservoir rocks. From their literature review, there was no definite result known about the effect of temperature on porosity. The bulk volume increases slightly (<1%) with temperature increase up to 200°C. However, a cubic pore model was analyzed to simulate the change in pore structure due to thermal expansion of mineral grains and cement. The expansion of the grain spheres and the quartz cement due to temperature increase was calculated using the thermal expansion coefficients of quartz. Different degrees of cementation were

considered in the model. Changes of pore radius at different temperature levels were obtained by subtracting new cement thickness from new grain radius. Vodak et al. (2004) studied the effect of temperature on strength-porosity relationship for concrete material at various temperatures ranging from 25 to 280°C. Their study depicted that the increment of porosity as a result of microcracking is mainly due to thermal incompatibility of hardened cement paste and aggregate during heating. Tian et al. (2004) obtained similar results in their experimental studies on sandstone, claystone, clayey sandstone, and sandy claystone where specimens were heated up to 1000°C. It was observed that cracks were generated on the rock samples, especially claystone, due to the difference in thermal expansion properties of different minerals in the rock. Yao et al. (2012) and Hu et al. (2012) presented further investigations on the microcracking mechanism during the procedure of heating rock and coal samples. In general, at the initial heating stage, the rise of temperature leads to the expansion of rock matrix, but the temperature is not high enough to generate microcracks. Therefore, at the initial heating stage, the porosity would slightly drop, or keep constant because of expansion of matrix and the inelastic property preventing restoration of deformation when specimens are cooled to ambient temperature. As the temperature continuously increases, the induced thermal stress reaches and exceeds the strength of matrix, thus leading to the generation of microcracks and increase of porosity. Therefore, a “threshold temperature” exists, where the sudden jump of porosity is observed, as the thermal stress becomes higher than the matrix strength and creates cracks in rocks. Yuan et al. (2012) conducted experimental study and simulated the effect of temperature on the voids in cement under high pressure and temperature conditions.

Second Category: Temperature Lower than Ice Melting Point

Other studies have paid attention to the effect of freezing on rock properties. Hundere (1984) investigated the changes of unconsolidated core properties after freezing. Kindt (1985) studied the effect of freezing on permeability of unconsolidated sandstone through experimental measurement. Torsaeter and Beldring (1987) analyzed the effect of freezing on the permeabilities of unconsolidated to slightly consolidated rocks and core plugs. Increment

in porosity, which ranges from 0.7% to 9.6%, was observed in their experimental data. Neaupane et al. (1999) presented a coupled thermo-hydro-mechanical model to simulate the freezing and thawing process. Their study focused on the effect of phase change of pore water on the deformation of material. No discussion of the change of porosity by freezing is available in the paper. Coussy (2005) studied the poromechanics of freezing materials with the focus on the liquid saturation degree as a function of temperature, and ice-dependent poroelastic properties.

From the descriptions above, most of the previous researches focused on the high temperature effect, or the effect of phase change of the pore water on the matrix structure in freezing process. The induced thermal stress due to freezing may result in fractures. It is expected that a "threshold temperature" exists during freezing, where sudden change of porosity due to fracturing would be observed. Some of aforementioned researches compared the rock or specimen porosity before and after freezing, and the porosity change with the variation of temperature. Unfortunately, it is unfeasible to measure shale porosity before freezing due to its brittle nature. To drill plug from shale core successfully, the core needs to be frozen. Therefore quantification of porosity change resulting from freezing is highly desirable for the sake of obtaining original shale porosity. In this study, the difference has been quantified in rock porosity before and after the freezing based on experimental data from numerous rock specimens. To do so, porosities of the samples were measured before

they were frozen. Then samples were stored in freezer and frozen at temperatures of -13.8 and -85°C for more than one week. After that they were taken out of freezer and allowed to return to temperature of 20°C. Their porosities were measured again once temperature reached equilibrium.

Equipment, Measurement Principle, and Procedure

Equipment

Gas compression method is used to measure the porosities of specimens in this work. Fig. 1 shows the setup to measure rock porosity. The system consists of gas source, three pressure gauges, and two chambers. The core is put in Chamber 2.

Measurement Principle

The measurement principle is based on real gas law. Followings are the derivation of governing equation to measure the core porosity.

Firstly, the sum of the volume of Chamber 1 and pipeline volume between Gas Inlet Valve and Gas Outlet Valve is denoted as Volume 1, V_1 .

$$V_1 = V_{\text{chamber 1}} + V_{\text{pipeline between Gas Inlet Valve and Gas Outlet Valve}} \quad (1)$$

Similarly, the sum of the volume of Chamber 2 (without core) and pipeline volume between Gas Outlet Valve and Gas Vent Valve is denoted as Volume 2, V_2 .

$$V_2 = V_{\text{chamber 2}} + V_{\text{pipeline between Gas Outlet Valve and Gas Vent Valve}} \quad (2)$$

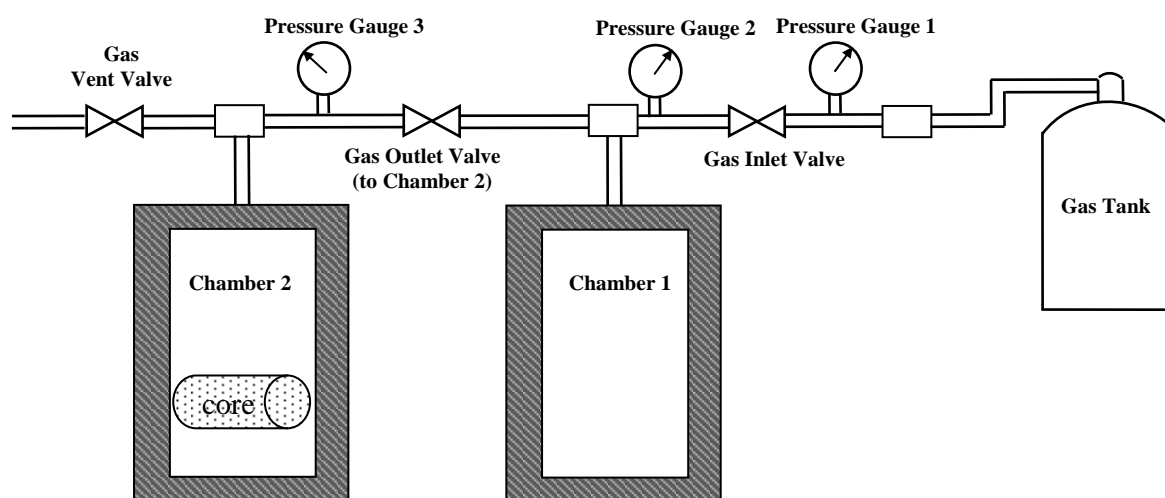


FIG. 1 SCHEMATIC OF FACILITY TO MEASURE ROCK POROSITY

The bulk volume of core is denoted as $V_{bulk, core}$ which is calculated by

$$V_{bulk, core} = \frac{\pi}{4} D_{core}^2 h_{core} \quad (3)$$

Initially, the pressure in Chamber 1 is p_1 and pressure in Chamber 2 is p_2 , where $p_1 > p_2$. Then Gas Outlet Valve is open to allow gas flow from Chamber 1 to Chamber 2 and reach equilibrium. The equilibrium pressure, p_3 , is recorded. According to real gas law we have

$$p_1 V_1 = z_1 n_1 R T_1 \quad (4)$$

$$p_2 [V_2 - V_{bulk, core} (1 - \phi)] = z_2 n_2 R T_2 \quad (5)$$

$$p_3 \{ [V_2 - V_{bulk, core} (1 - \phi)] + V_1 \} = z_3 (n_1 + n_2) R T_3 \quad (6)$$

The temperature is kept constant and pressure is changed in a narrow range. Therefore we have

$$z_1 \cong z_2 \cong z_3 \quad (7)$$

Equations (4), (5), and (6) can be simplified into

$$p_1 V_1 = z_1 n_1 R T_1 \quad (8)$$

$$p_2 [V_2 - V_{bulk, core} (1 - \phi)] = z_1 n_2 R T_1 \quad (9)$$

$$p_3 \{ [V_2 - V_{bulk, core} (1 - \phi)] + V_1 \} = z_1 (n_1 + n_2) R T_1 \quad (10)$$

Summing Equations (8) and (9) we obtain

$$p_2 [V_2 - V_{bulk, core} (1 - \phi)] + p_1 V_1 = z_1 (n_1 + n_2) R T_1 \quad (11)$$

Comparing the right-hand-sides of Equations (10) and (11) we have

$$p_2 [V_2 - V_{bulk, core} (1 - \phi)] + p_1 V_1 = p_3 \{ [V_2 - V_{bulk, core} (1 - \phi)] + V_1 \} \quad (12)$$

Rearranging Equation (12) yields

$$\phi = 1 - \frac{V_2}{V_{bulk, core}} + \frac{(p_1 - p_3) V_1}{(p_3 - p_2) V_{bulk, core}} \quad (13)$$

Equation (13) is the governing equation to measurement rock porosity. Three pressures are recorded in the measurement. Volume 1, V_1 , and Volume 2, V_2 can be determined using standard volume samples made of stainless steel (zero porosity). The approach is also based on real gas law. The bulk volume of core can be readily calculated from core diameter and height.

Measurement Procedure

The measurement of porosity of a specimen includes following steps:

- 1) Put the core into Chamber 2, close Gas Vent Valve, and open Gas Inlet Valve and Gas Outlet Valve to allow gas from gas tank fill Chambers 1 and 2 until pressure reaches 100 psig
- 2) Open Gas Vent Valve and allow gas from gas tank purge Chambers 1 and 2, keeping 10 to 20 minutes until the purity of gas in Chambers 1 and 2 is high enough.
- 3) Close Gas Vent Valve, Gas Inlet Valve, and Gas Outlet Valve, record the pressure of Chamber 2, p_2 .
- 4) Keep Gas Vent Valve and Gas Outlet Valve close, Open Gas Inlet Valve and allow gas from gas tank fill Chamber 1 until its pressure reaches target pressure, close Gas Inlet Valve and record the pressure of Chamber 1, p_1 .
- 5) Open Gas Outlet Valve to allow gas flow from Chamber 1 to Chamber 2 (because $p_1 > p_2$), wait until pressure reaches equilibrium, or pressure at Pressure Gauge 3 equates pressure at Pressure Gauge 2, record equilibrium pressure, p_3 .
- 6) Now the porosity measurement of specimen has been completed. Porosity can be calculated by Equation (13).

Two series of different size specimens were used in this work, the first of which has a dimension of 1-in. diameter by 2-in. length, and another has a dimension of 2-in. in diameter by 4-in. in length. The porosities of rock before and after freezing were measured. The procedure of our experiment is:

- 1) Measure the porosity of rock at temperature of 20 °C before frozen.
- 2) Put the specimen into freezer and freeze it at temperature of -13.8°C for one week, then take it out of freezer and allow specimen temperature return to 20°C. Then measure specimen porosity again.
- 3) Put the specimen into another freezer and freeze it at temperature of -85°C for one week, then take it out of freezer and allow specimen temperature return to 20°C. Then measure specimen porosity

one more time.

Upon finishing the procedure we obtain three porosities for each specimen: one before freezing, one after freezing at -13.8°C , and one after freezing at -85°C .

Experimental Results Analysis and Development of Correlations

To demonstrate the change of porosity by freezing distinctly, the relative porosity change is calculated using porosity of rocks at 20°C as the base. Table 1 shows the experiment results.

Based on the test data, three kinds of porosity change by freezing can be identified as shown in Fig. 2, and correspond to different types of rocks. For the first type (a), whose lithology is shaly sandstone, the porosity increases as the rock has been frozen, and reaches maximum at temperature barely lower than zero. After that, local maximum, porosity declines as temperature is reduced further. For the second type (b), whose lithology is clean sandstone, the trend is similar to first type but with smaller change. The porosity change by freezing is very small until temperature reaches the "threshold temperature", beyond that point the porosity begins to increase quickly. The third type (c), whose lithology is sandstone with high calcium carbonate concentration, follows the same trends as first and second types. A local maximum porosity is seen at temperature barely lower than zero, but the change of porosity lies between first and second types. A "threshold temperature" also can be found as the temperature decreases continuously. When the temperature is lower than the "threshold temperature", the porosity increases again.

Three equations corresponding to three rock types are listed below:

a:

$$y = -2.6 \times 10^{-6} x^3 - 4.0 \times 10^{-4} x^2 - 1.13 \times 10^{-2} x + 0.48 \quad (14)$$

b:

$$y = -3.6 \times 10^{-7} x^3 - 2.2 \times 10^{-5} x^2 + 7.6 \times 10^{-5} x + 0.01 \quad (15)$$

c:

$$y = -2.9 \times 10^{-6} x^3 - 2.0 \times 10^{-4} x^2 + 3.4 \times 10^{-3} x + 0.049 \quad (16)$$

where x is temperature and y is the relative porosity change.

Discussions

Porosity change is the combined effects of expansion of the water inside the core due to phase change and the contractions of the matrix of the core and ice. When the core is stored in freezer at temperature lower than freezing point, the freezing causes the water inside the core to expand due to the fact that ice occupies a larger volume than liquid water. The relative volume change is

$$\frac{\Delta V_{\text{expansion}}}{V_{\text{water}}} = \frac{V_{\text{ice}} - V_{\text{water}}}{V_{\text{water}}} = 8.7\% \quad (17)$$

The expansion volume due to water phase change is

$$\Delta V_{\text{expansion}} = 0.087 V_{\text{water}} = 0.087 \phi S_w V_{\text{bulk,core}} \quad (18)$$

During the freezing both ice and rock matrix contract. The volume change due to the contraction can be estimated using the thermal expansion coefficient. The contraction volumes of ice and rock matrix are calculated by

$$\begin{aligned} \Delta V_{\text{contraction,ice}} &= V_{\text{ice}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{\text{ice}} \\ &= 1.087 \phi S_w V_{\text{bulk,core}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{\text{ice}} \end{aligned} \quad (19)$$

and

$$\begin{aligned} \Delta V_{\text{contraction,matrix}} &= \sum_i^n V_{i,\text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i,\text{mineral}} \\ &= V_{\text{bulk,core}} (1 - \phi) \sum_i^n f_{i,\text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i,\text{mineral}} \end{aligned} \quad (20)$$

respectively.

where

$$\alpha_{\text{ice}} = 50 \times 10^{-6} \text{ } 1/^{\circ}\text{C}$$

and the coefficients of thermal expansion of different minerals are listed in Table 2.

Combining Equations (18), (19), and (20) we have the total volume change, which is

$$\begin{aligned} \Delta V_{\text{total}} &= \Delta V_{\text{contraction,ice}} + \Delta V_{\text{contraction,matrix}} - \Delta V_{\text{expansion}} \\ &= V_{\text{bulk,core}} \left[\begin{aligned} &1.087 \phi S_w (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{\text{ice}} \\ &+ (1 - \phi) \sum_i^n f_{i,\text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i,\text{mineral}} \\ &- 0.087 \phi S_w \end{aligned} \right] \end{aligned} \quad (21)$$

TABLE 1 SPECIMEN DATA AND CHANGE OF POROSITY CAUSED BY FREEZING

Samples	Diameter	Length	Porosity Φ (%)			$(\Phi - \Phi_{20})/\Phi_{20}$		
	mm	mm	20 °C	-13.8 °C	-85 °C	20 °C	-13.8 °C	-85 °C
1	23.54	42.25	12.512	19.197	14.127	0.000	0.534	0.129
2	24.3	51.55	10.969	14.472	14.579	0.000	0.319	0.329
3	24.65	28.44	16.624	21.496	18.006	0.000	0.293	0.083
4	24.69	49.98	11.296	13.764	12.620	0.000	0.218	0.117
5	24.25	52.58	12.755	14.770	13.886	0.000	0.158	0.089
6	24.38	52.69	13.504	14.968	14.168	0.000	0.108	0.049
7	24.67	55.25	16.481	17.941	18.068	0.000	0.089	0.096
8	24.69	52.6	13.501	14.694	14.470	0.000	0.088	0.072
9	24.95	51.05	18.478	20.029	18.870	0.000	0.084	0.021
10	24.73	51.56	18.807	20.302	19.698	0.000	0.079	0.047
11	24.82	51.55	15.057	15.976	15.531	0.000	0.061	0.031
12	38.44	76.15	13.999	14.759	14.574	0.000	0.054	0.041
13	24.65	58.38	17.068	17.952	17.770	0.000	0.052	0.041
14	38.08	74.33	12.958	13.583	13.784	0.000	0.048	0.064
15	38.43	76	13.382	14.006	13.832	0.000	0.047	0.034
16	38.43	76.26	14.868	15.534	15.574	0.000	0.045	0.047
17	24.45	53.91	22.483	23.485	23.491	0.000	0.045	0.045
18	38.48	76.18	12.114	12.652	12.090	0.000	0.044	-0.002
19	38.42	76.25	13.699	14.209	14.493	0.000	0.037	0.058
20	38.25	75.21	13.212	13.646	13.804	0.000	0.033	0.045
21	38.47	74.14	13.728	14.125	13.931	0.000	0.029	0.015
22	24.76	46.6	12.995	13.364	14.038	0.000	0.028	0.080
23	38.38	75.77	13.778	14.138	13.951	0.000	0.026	0.013
24	25	51.95	15.194	15.569	16.415	0.000	0.025	0.080
25	38.42	76.26	13.802	14.134	14.209	0.000	0.024	0.029
26	24.63	50.37	22.060	22.566	24.060	0.000	0.023	0.091
27	24.81	49.62	15.094	15.311	15.583	0.000	0.014	0.032
28	38.44	76.05	14.238	14.350	14.268	0.000	0.008	0.002
29	24.3	52.37	12.875	12.953	15.676	0.000	0.006	0.218
30	24.27	52.95	17.583	17.684	18.736	0.000	0.006	0.066
31	50.12	102.78	14.963	15.028	14.905	0.000	0.004	-0.004
32	38.47	76.14	12.412	12.426	12.603	0.000	0.001	0.015
33	50.27	105.05	15.611	15.591	15.491	0.000	-0.001	-0.008
34	38.3	75.81	13.334	13.279	13.177	0.000	-0.004	-0.012
35	38.2	76.15	13.547	13.453	13.512	0.000	-0.007	-0.003
36	50.16	102.78	15.057	14.910	14.936	0.000	-0.010	-0.008
37	25.68	50.31	21.884	21.660	22.118	0.000	-0.010	0.011
38	50.24	103.43	15.681	15.510	15.562	0.000	-0.011	-0.008
39	38.46	76.03	14.976	14.803	14.600	0.000	-0.012	-0.025
40	38.35	76.25	14.156	13.959	14.192	0.000	-0.014	0.003
41	38.46	78.17	16.881	16.635	16.845	0.000	-0.015	-0.002
42	24.78	50.78	16.586	16.338	16.901	0.000	-0.015	0.019
43	24.47	48.81	11.164	10.917	15.535	0.000	-0.022	0.392
44	24.84	48.97	15.599	15.234	15.533	0.000	-0.023	-0.004
45	38.45	76.15	14.352	13.970	13.954	0.000	-0.027	-0.028
46	24.5	52.55	15.155	14.658	15.408	0.000	-0.033	0.017
47	24.08	51.48	15.224	14.713	15.698	0.000	-0.034	0.031
48	24.17	50.09	9.821	9.386	13.411	0.000	-0.044	0.366
49	24.74	51.49	16.681	15.858	17.042	0.000	-0.049	0.022
50	24.58	51.65	13.062	12.199	15.665	0.000	-0.066	0.199
51	24.83	51.85	16.718	15.605	16.960	0.000	-0.067	0.014
52	24.8	50.45	15.283	14.235	17.547	0.000	-0.069	0.148
53	24.65	52.67	12.503	11.583	15.378	0.000	-0.074	0.230
54	24.17	50.45	11.694	10.684	13.892	0.000	-0.086	0.188
55	24.4	52.27	11.843	10.799	13.288	0.000	-0.088	0.122
56	24.25	52.56	13.886	12.305	16.040	0.000	-0.114	0.155

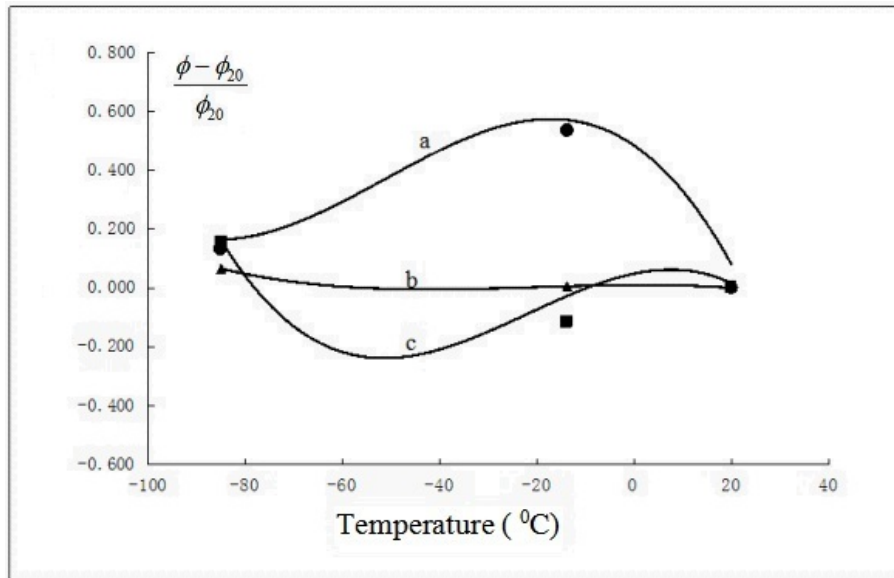


FIG. 2 REGRESSION ANALYSIS OF CHANGE OF POROSITY CAUSED BY FREEZING

TABLE 2 THERMAL EXPANSION COEFFICIENTS OF COMMON MINERALS IN ROCK

Mineral	Thermal Expansion Coefficient	Reference
Quartz	$0.77\sim 1.4\times 10^{-6} \text{ } 1/^{\circ}\text{C}$	http://www.engineeringtoolbox.com/linear-expansion-coefficients-d_95.html
Alkali Feldspar	$14\sim 17\times 10^{-6} \text{ } 1/^{\circ}\text{C}$	Hovis, G., et al., 2008, A simple predictive model for the thermal expansion of AlSi_3 feldspars.
Plagioclase Feldspar	$10\sim 17\times 10^{-6} \text{ } 1/^{\circ}\text{C}$	Tribaudino, M., et al., 2010, Thermal expansion of plagioclase feldspars:
Calcium Carbonate	$6\sim 9\times 10^{-6} \text{ } 1/^{\circ}\text{C}$	http://www.supercivilcd.com/THERMAL.htm
Calcium Carbonate	$8\times 10^{-6} \text{ } 1/^{\circ}\text{C}$	http://www.engineeringtoolbox.com/linear-expansion-coefficients-d_95.html

Therefore, the relative volume change is

$$\frac{\Delta V_{total}}{V_{bulk, core}} = \left[\begin{array}{l} 1.087\phi S_w (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{ice} + \\ (1-\phi) \sum_i^n f_{i, \text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i, \text{mineral}} \\ -0.087\phi S_w \end{array} \right] \quad (22)$$

Equation (22) gives the incremental porosity at freezer temperature. So the rock porosity at freezer temperature is

$$\phi_{\text{freezer temperature}} = \left[\begin{array}{l} 1.087\phi S_w (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{ice} \\ + (1-\phi) \sum_i^n f_{i, \text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i, \text{mineral}} \\ -0.087\phi S_w \end{array} \right] \quad (23)$$

If the induced stress is less than the adhesive strength of rock and the rock is elastic, the rock should restore to its original condition when the temperature is restored to original temperature. Unfortunately, no

rock is completely elastic. Therefore, rock cannot restore to its original condition exactly even the rock is not damaged by the induced stress. The residual porosity difference as a result of freezing-unfreezing cycle depends on the water and the percentage of inelastic component in rock.

If the induced stress is higher than the adhesive strength of rock, rock porosity after freezing-unfreezing cycle will be larger than the original porosity because the microcracks and plastic component in the rock prevent the rock from restoring to original condition when temperature return to original value. To evaluate the occurring of microcrack, it is necessary to introduce the definition of volumetric strain, which is defined as the ratio of the change in volume of the body to its original volume (Jaeger, et al., 2007).

$$\varepsilon_v = \frac{\Delta V}{V_{\text{original}}} \quad (24)$$

Recalling that the volumetric strain is the sum of the three principal normal strains, we have

$$\varepsilon_V = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (25)$$

The relationships between the three principal normal stresses and strains give us

$$\sigma_1 = \lambda \varepsilon_V + 2G \varepsilon_1 \quad (26)$$

$$\sigma_2 = \lambda \varepsilon_V + 2G \varepsilon_2 \quad (27)$$

$$\sigma_3 = \lambda \varepsilon_V + 2G \varepsilon_3 \quad (28)$$

Summing up the three principal stresses gives

$$3\tau_m = \sigma_1 + \sigma_2 + \sigma_3 = (3\lambda + 2G) \varepsilon_V \quad (29)$$

The mean stress is related to the volumetric strain through

$$\tau_m = \left(\lambda + \frac{2}{3}G \right) \varepsilon_V$$

$$= \left(\lambda + \frac{2}{3}G \right) \left[\begin{array}{l} 1.087\phi S_w (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{\text{ice}} + \\ (1-\phi) \sum_i^n f_{i,\text{mineral}} (T_{\text{freezing point}} - T_{\text{freezer}}) \alpha_{i,\text{mineral}} \\ -0.087\phi S_w \end{array} \right] \quad (30)$$

where

$$\lambda = \frac{2G\nu}{1-2\nu} \quad (31)$$

If the mean stress calculated from Equation (30) is higher than adhesive strength of rock, microcrack will be created and increase in porosity will be expected.

Analysis of experimental data indicates that there is a "threshold temperature" for rock. When the rock is frozen at temperature high than "threshold temperature" and restored to original temperature, porosity decreases. Otherwise, porosity increases. At temperature between freezing point and "threshold temperature", the expansion resulting from phase change from water to ice dominates over the contractions of rock matrix and ice. The expanded volume is larger than the contracted volume. The deformation occurring at this temperature range is partially inelastic and the rock cannot restore to original condition even temperature is restored to original temperature. It should be noted that the induced stress is below the adhesive strengths between cements and grains or the strength of matrix under this temperature range. At temperature lower than the "threshold temperature", the contractions of ice and rock matrix dominates over the expansion due to the water phase change. The induced thermal stress resulting from strain caused by contraction reaches

and exceeds the adhesive strengths between cements and grains or the strength of matrix, thus leading to the creation of microcracks. These microcracks are the main reason for the increment of porosity. Under such condition, the expanded volume is smaller than the contracted volume. The deformation is damaging and irreversible, and again the rock cannot restore to its original condition after temperature is restored to original temperature. Obviously, the "threshold temperature" is a function of rock type, rock structure, texture, mineral composition, rock strength, water saturation, mineral hydration, and porosity. To calculate an accurate porosity change, it is necessary to know the volumetric fraction of minerals in rock, as well as the coefficient of thermal expansion of each mineral.

Conclusions

Following conclusions can be drawn upon finishing this study:

There is a "threshold temperature" for every specific rock. If the rock is frozen at temperature high than "threshold temperature", porosity will decrease. Otherwise, porosity will increase.

The "threshold temperature" is a function of rock type, rock structure, texture, mineral composition, rock strength, water saturation, mineral hydration, and porosity.

At temperature between freezing point and "threshold temperature", the expansion resulting from water phase change to ice dominates over the contraction of rock matrix. The expanded volume is larger than the contracted volume. The deformation occurring at this temperature range is partially inelastic and the rock cannot restore to original condition completely even temperature is restored to original value.

At temperature lower than the "threshold temperature", the contractions of ice and rock matrix dominates over the expansion due to the water phase change. The stress resulting from strain caused by contraction exceeds the adhesive strengths between cements and grains, thus leading to the creation of microcracks which are the main reason of the increase in porosity. Under such condition, the expanded volume is smaller than the contracted volume. The deformation is damaging and irreversible, and again the rock cannot restore to original condition after temperature is returned to original value.

Three empirical correlations related to three rock types

have been developed to estimate the porosity change before and after freezing.

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NOMENCLATURE

D_{core}	= core diameter
$f_{i,mineral}$	= volumetric fraction of mineral i in total matrix
G	= shear modulus
h_{core}	= length of core
n_1	= gas moles in Chamber 1
n_2	= gas moles in Chamber 2
p_1	= pressure at Chamber 1
p_2	= pressure at Chamber 2
p_3	= pressure at Chambers 1 and 2 after pressure reaches equilibrium
R	= universal gas constant
S_w	= water saturation
T_1	= temperature at Chamber 1
T_2	= temperature at Chamber 2
T_3	= temperature at Chambers 1 and 2 after pressure reaches equilibrium
$T_{freezer}$	= freezer temperature
$T_{freezing\ point}$	= water freezing temperature
V_1	= volume of chamber 1 + pipeline volume between Gas Inlet Valve and Gas Outlet Valve
V_2	= volume of chamber 2 (without core) + pipeline volume between Gas Outlet Valve and Gas Vent Valve
$V_{chamber\ 1}$	= volume of chamber 1
$V_{chamber\ 2}$	= volume of chamber 2 (without core)
$V_{bulk,\ core}$	= bulk volume of core

V_{ice}	= ice volume
$V_{original}$	= original volume
$V_{pipeline\ volume\ between\ Gas\ Inlet\ Valve\ and\ Gas\ Outlet\ Valve}$	= pipeline volume between Gas Inlet Valve and Gas Outlet Valve
$V_{pipeline\ volume\ between\ Gas\ Outlet\ Valve\ and\ Gas\ Vent\ Valve}$	= pipeline volume between Gas Outlet Valve and Gas Vent Valve
V_{water}	= water volume
ν	= Poisson's ratio
z_1	= gas z-factor at Chamber 1
z_2	= gas z-factor at Chamber 2
z_3	= gas z-factor at Chambers 1 and 2 after pressure reaches equilibrium
ΔV	= volume change
$\Delta V_{expansion}$	= expansion volume due to water phase change
$\Delta V_{contraction, ice}$	= ice contraction volume
$\Delta V_{contraction, matrix}$	= matrix contraction volume
$\Delta V_{i, mineral}$	= mineral i contraction volume
ΔV_{total}	= total volume change
α_{ice}	= coefficient of thermal expansion of ice
$\alpha_{i, mineral}$	= coefficient of thermal expansion of mineral i
ϕ	= porosity, or original porosity
$\phi_{freezer\ temperature}$	= porosity at freezer temperature
$\phi_{original}$	= original porosity
ϵ_1	= first principal normal strain
ϵ_2	= second principal normal strain
ϵ_3	= third principal normal strain
ϵ_V	= volumetric strain
σ_1	= first principal normal stress
σ_2	= second principal normal stress
σ_3	= third principal normal stress
τ_m	= mean stress

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